Delocalized and correlated wave functions for excited states in extended systems

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Theoretical Framework

"If quantum mechanics hasn't profoundly shocked you, you haven't understood it yet"

Niels Henrik David Bohr

2.1 The embedded cluster approach

2.1.1 Introductory remarks

As an alternative to the conventional band structure description of crystalline materials a different approach can be considered which is based on modeling the solid by a small collection of atoms at lattice positions of the system, a cluster, embedded in a potential which accounts for the part of the crystal that is not explicitly included in the cluster. This approach is well known as the embedded cluster approach.

In this thesis the embedded cluster approach is employed as a starting point in the studies of excited, ionized and added-electron states of insulating crystalline transition metal materials. In studying excited or ionized and added-electron states with mainly localized character the local cluster approach is a more common starting point than the conventional band theory. It has been shown by Nieuwpoort and Broer [1] that in the case of closed-shell ionic systems, the ground state wave functions derived from large enough embedded clusters and the corresponding crystal Wannier functions obtained both at the Hartree-Fock level are in fact equivalent. This is not the case for ionized or added-electron systems where the large electronic relaxation effects which accompany the ionization and electron addition process are not incorporated in the delocalized description. The electronic relaxation effects can be well defined for hole states and added-electron states. We consider an N -electron system, described by an N -electron wave function. The latter is considered to be multi-configurational SCF wave function. When an electron is removed from the N -electron wave function without any further changes in the wave function, the resulting *N-1* -electron wave

function is denoted as unrelaxed, frozen wave function. This wave function can be optimized within the variational principle in order to obtain the best wave function for the *N-1* -electron system. The changes in the *N-1* -electron wave function (orbitals and configuration interaction coefficients) that occur when the wave function becomes the optimal wave function for the *N-1* -electron system are called electronic relaxation. When a hole or an electron is created in a very localized, almost atom-like state, the relaxation energy gain is substantial. In the band description, for instance, the hole is created in a Bloch state at the top of a band with a particular predominant character. Because the hole-orbital is delocalized over all translation symmetry invariant lattice sites of a certain type, the change in the electron density at each site is vanishingly small and hence, no orbital relaxation takes place (Koopmans' Theorem is valid) [1]. In a cluster description the hole is created in the highest occupied orbital with the same predominant character, however it is localized, thus allowing for the electronic relaxation. Therefore for those processes, the local approach provides a better description. In addition the embedded cluster model facilitates the inclusion of electron correlation effects because it allows for an *ab initio* many-body description of the electronic wave functions using state-of-the-art quantum mechanical wave function based techniques.

As shown in numerous studies on local excitations in transition metal materials (see [2–6] and the references therein), core level excitations (*e.g.* [7,8]), magnetic couplings and hopping integrals between localized states [9–12, 14, 15], the cluster model combined with an accurate quantum-mechanical wave-function based treatment of the cluster electrons allows for an accurate account for the local correlation and relaxation effects. X-ray absorption, photo-emission, photo-electron, core X-ray photo-emission *etc.* spectra of various TM materials [3, 19–22] are described accurately using the local cluster approach.

In the cluster approach, the effective cluster Hamiltonian must be modified to incorporate both the electrostatic interactions with the charges outside the cluster region and the fact that the electrons described by the cluster wave function are not confined to the cluster in the real crystal, i.e. the cluster wave functions may extend beyond the cluster region [23]. It is clear that while for ionic compounds the electrostatic interactions have more significance than the extension of the cluster wave functions beyond the boundaries of the cluster, for covalent structures the importance of these effects is *vice versa*.

In covalent materials and metals, the electrostatic interactions decrease fast with the distance from the cluster region due to the effective screening processes (particularly metals). In ionic solids, however, the electrostatic fields have a long range. Most often the interactions between the cluster and surrounding crystal are classified as long-range and short-range electrostatic interactions. In addition long-range polarization effects are of a great importance, for example, for charged defects in ionic crystals.

Different embedding techniques have been developed in the last decades to facilitate the incorporation of the electrostatic interactions between the cluster region and the surrounding crystal in the electronic structure calculations. Some of them, devel-

oped mainly for ionic materials, the *Ab Initio* Model Potential (AIMP) method, by Barandiarán and Seijo [24] and others, based on the so-called effective core potential technique by Hay and Wadt [25], have been employed in this thesis and thus, will be summarized briefly in the next sections.

2.1.2 Long- and short-range electrostatic interactions

As stated above, the electrostatic interactions between the cluster and surrounding lattice are formally divided into long-range and short-range electrostatic interactions. The long-range interactions are of importance mostly for the ionic materials. They are usually included in the local model by adding the Madelung potential generated by all ions outside the cluster region to the cluster effective Hamiltonian. This is done by first calculating the Madelung potential using infinite lattice sums which are easily handled by the Ewald summation method [26]. The Ewald summation is performed using point charges at experimental lattice positions. Next the cluster contribution to the total potential is subtracted in order to obtain the external Madelung potential. In practical calculations, the external Madelung potential may be obtained by performing a summation over the contributions of a large enough set of point charges at lattice positions aiming at the exact value of the external Madelung potential to some predefined accuracy. Because of the slow convergence of the Madelung potential with the distance, this approach is not practical since it requires a large set of formal point charges. The approach used in this thesis is based on a fitting procedure using the least squares numerical method. A finite (usually rather small) set of point charges at lattice positions within a certain range around the cluster are optimized within the fitting procedure in order to obtain the closest to the exact value of the Madelung potential on a fine grid within the cluster region. This approach has, for example, been exploited extensively by Janssen [27] and de Graaf [28].

The short-range interactions can not be treated using classical models. They consist of Pauli repulsions supplemented by Coulomb and exchange interactions between the cluster charge distributions and the charge distributions of its nearest neighbouring ions. The modeling of these interactions has been a subject of long-term studies and many various approaches have been suggested and developed [24,30,34–41,46,53].

The embedded cluster approach, subject of the current discussion, can be derived starting from one of those approaches, the Theory of the electron separability (*TES*)) in combination with the Group-Function Theory (*GFT*) [24, 30, 46]. These two theories are also the starting point for the derivation of the embedding model potentials that are employed in this thesis. In this study we consider excitations, ionizations and electron additions in insulating transition metal compounds using crystal lattices of the compounds with ions for which formal ionic charges are adopted at first approximation. When designing the cluster, which in the present study contains one or few transition metal ions and the coordinating shells of O^{2-} ions, one must take into consideration that the nearest embedding shells of ions around the cluster are best represented by effective model potentials. This requirement holds especially for the positive embedding ions nearby the cluster counterions, because a point charge repre-

sentation of those cations may result in an artificial polarization of the cluster orbitals towards the positive point charges (see also below). Because we use extensively in this thesis the model potential techniques which are derived from the consideration of the *TES* and *GFT*, we adopt the same line of presentation of the formalism of the embedded cluster approach, although the embedded cluster approach can be considered without referring to the *TES* and *GFT*.

The simplest way to account for the rest of the crystal surrounding the cluster is to account only for the long-range electrostatic potential by introducing corresponding point charges at lattice positions. For very ionic materials such cluster models turn out to be rather accurate because the electronic states have predominantly localized character (*e.g.* Ref. [2, 7]). Furthermore the dependence of the energies of localized excited, ionized or added-electron states on the cluster size can be accounted for by enlarging the cluster (for example [64]). The size of the cluster required to study states with predominantly localized character in materials with covalency, is usually small enough to be handled computationally. However, representing the short-range Coulomb interactions between the cluster and embedding ions by point charges as it has been done in earlier studies (see for example [44]) may introduce problems, such as delocalization of the cluster wave function towards the point charges. This problem is particularly emphasized in the case of an ionic material for which the model cluster has embedding ions (for example La^{3+}, Y^{3+}, Ge^{4+}) with high formal ionic charges (see, for example, [45]). In order to avoid the artificial charge flow the Pauli repulsion between cluster and nearest embedding ions must be taken into account. A natural way to do this is to introduce repulsive potentials set at those nearby ions.

In case of a material with a greater degree of covalency, the studies of localized excited, ionized states or impurities can be carried out for sufficiently large clusters terminated using appropriate termination schemes. For instance, Aissing has shown in his study of the band width, band gap, ionization energy and electron affinity of pure silicon, that these quantities can be extrapolated from clusters with an increasing size in order to account for the cluster artifacts [31, 32, 89]. Some of the clusters in that study are Si_5H_{12}, $Si_{10}H_{16}$, $Si_{17}H_{36}$, clusters. The H atoms are used to saturate the dangling bonds of the surface Si atoms. In studies of, for example, transition metal impurities in Si [31, 89], this is a simplistic but an efficient way to handle the so called surface states, which are due to the dangling bonds of the surface Si atoms.

Theory of the electron separability and Group-Function Theory

Since the short-range electrostatic interactions are object of quantum mechanical treatment, different quantum chemical approaches are developed to incorporate them in the local model. One of those methods is based on the so-called theory of electron separability (*TES*) [30, 53]. The *TES* formalism uses conventional wave function based methods for finite systems to describe the properties of extended structures. The approach is denoted as Group-Function Theory (*GFT*) and it is developed by McWeeny and Kleiner [46] and Huzinaga and Cantu [30, 53].

The Theory of the Electron Separability assumes that it is possible to partition the extended system into various electronic groups I, S, ..., each containing a number

of electrons N_I, N_S, ... The groups electronic states a, b, ... are described by the antisymmetric group wave functions Φ_a^I, Φ_b^S, ... [24, 46]. The wave functions Φ_κ for the extended system are then constructed as generalized antisymmetrized products of the wave functions $\Phi_x^X(\mathbf{r_1}, \mathbf{r_2}, ..., \mathbf{r_{N_X}})$ [24, 46]:

$$\Phi_\kappa(\mathbf{r_1}, ..., \mathbf{r_N}) \quad = \quad \hat{A} M_\kappa [\Phi_a^I(\mathbf{r_1}, ..., \mathbf{r_{N_I}}) \Phi_b^S(\mathbf{r_{N_I+1}}, ..., \mathbf{r_{N_I+N_S}}) ....] \qquad (2.1)$$

where N=(N_I+N_S+ ...) $\rightarrow \infty$ and M_κ is a normalization factor and $\hat{A}$ is the intergroup antisymmetrizer. Φ_κ corresponds to a particular configuration of states for the different electron groups, namely, κ= (IaSb...). This wave function representation allows one to include in a straightforward manner the electron correlation locally within each electron group I, since Φ_a^I can be a MC wave function expansion. This flexibility of the *GFT* is exploited by the embedded cluster approach, where the electronic structure of one particular electronic group, the cluster, is described by a complicated MC wave function expansion while the surrounding lattice is treated with the frozen electron distribution.

Electron correlations between different electron groups I and S are not considered and therefore, they should not be relevant to the properties under investigation. In the case of weakly interacting electron groups, the approximate form (2.1) to the wave function of the extended system is well suited. In case the different electronic groups must be represented by more than one electronic state *a*, the wave function of the extended system may be written as a linear combination of different generalized product wave functions of the form (2.1):

$$\Psi_m \quad = \quad \sum_\kappa c_\kappa \Phi_\kappa \qquad (2.2)$$

One of the main approximations in GFT are the so-called *strong orthogonality conditions* which are imposed between the different electronic groups. These so-called strong orthogonality conditions are expressed as [24, 46],

$$\int \Phi_a^{*I}(\mathbf{r_1}, ..., \mathbf{r_{N_I}}) \Phi_{b,ex}^S(\mathbf{r_1}, \mathbf{r_{N_I+2}}, ..,) d\mathbf{r_1} = 0 \quad (I \neq S), \quad (a \neq b) \quad or \quad both. \quad (2.3)$$

where $\Phi_{b,ex}^S$ is the wave function obtained from Φ_b^S by exchanging one (or more) of its electron (s) with electron (s) of Φ_a^I. The integration is over the coordinates of that electron.

The zero overlap in Eq. (2.3) can be achieved by constructing the different electronic group wave functions from different and mutually orthogonal spin-orbital sets. McWeeny has shown that if a strong orthogonality condition is imposed, one can apply the generalized Slater method to the generalized product wave functions in Eq. (2.1), that allows one to handle the matrix elements of the crystal Hamiltonian, $\hat{H}$, between different product wave functions (2.1) as the matrix elements between antisymmetrized orbital products [46]. The mathematical formulation of *GFT* is presented in reference [46].

Very often the physical properties of the extended system can be ascribed to a particular electron group I, the cluster, and the effect of the remaining electron

groups S is regarded to be somewhat smaller. Then the detailed electronic structure of the groups S is not considered and the computational effort is redirected towards an accurate MC expansion of the wave function Φ_a^I of cluster I, whereas adopting the frozen electron distribution for all S groups, the latter are in their ground state '0', Φ_0^S. The complicated set of SCF equations for the N-electron (N$\rightarrow\infty$) system is reduced to a set of SCF equations for the cluster I in the effective field of all S$\neq$ I which represent the embedding of the cluster. The effect of the effective field is incorporated through the effective one-electron cluster Hamiltonian,

$$\begin{aligned}
\hat{h}_{eff}^I(i) &= \sum_{i\in I}\{-\frac{1}{2}\nabla_i^2 - \sum_\mu \frac{Z_\mu}{|\mathbf{r_i}-\mathbf{R}_\mu|} + \sum_{S(\neq I)}[\hat{J}^S(i)-\hat{K}^S(i)]\} \\
\hat{J}^S(i) &= \langle\Phi_b^S|\sum_{j\in S}\frac{1}{\mathbf{r_{ij}}}|\Phi_b^S\rangle \\
\hat{K}^S(i) &= \langle\Phi_b^S|\sum_{j\in S}\frac{\hat{P}(i,j)}{\mathbf{r_{ij}}}|\Phi_b^S\rangle
\end{aligned} \tag{2.4}$$

where the summation over μ is extended to all the nuclei of the system. Z is the nuclear charge. The effective one-electron Coulomb and exchange operators $\hat{J}^S(i)$ and $\hat{K}^S(i)$ in Eq. (2.4), however, are not used in practice in this form due to computational deficiencies [24]. The latter can be circumvented by replacing the embedding operators by model potentials which approximate the effect of the embedding on the cluster electron distributions [24, 25].

As mentioned in the introduction, various embedding techniques have been suggested and developed [24, 33, 34, 40–43]. Within the framework of this thesis we made use of two model potential techniques, namely the *Ab Initio* Model Potential method [24] and the Total Ion Potential Technique based on the effective core potential technique by Hay and Wadt [25]. In the next subsection, we outline the basics of the two techniques.

The *GFT* and *TES* formalisms have been considered here in connection with the embedded cluster approach, but they may be also applied to other systems for which it is possible to distinguish well -separated electron groups. For instance, the formalism is well suited to study inter-molecular fields, since they concern the interactions between two well-separated electron groups, which belong to two or more molecules. The applicability of those theories may be extended to describe also the solvent-solute dynamics [55, 56].

Furthermore, when considering the properties of a molecule which can be mainly ascribed to its valence electrons, the valence molecular wave function Φ_a^I may be constructed assuming frozen core-electron closed-shell atomic wave functions. Huzinaga and co-workers [34, 47] developed atomic model potentials to approximate the core-electron density distribution in valence-only calculations.

Embedding techniques

The straightforward employment of the embedding effective one-electron operators, that represent the crystal environment requires the computation of the same number of two-electron integrals as that needed when the system is treated as a whole [24]. Therefore, various techniques were implemented that aim at the representation of the local and non-local effective one-electron operators by model potentials [24]. One possible representation of the embedding operators is within the AIMP approximation of Seijo and Barandiarán [24].

The Ab Initio Model Potential approximation The AIMP method was initially developed by Huzinaga *et al.* to represent the core-electrons distribution in valence-only calculations [34, 47]. In order to replace the embedding operators associated with the electron groups S by appropriate embedding potentials, one may consider the long- and short- range Coulomb interactions and the exchange interaction of the cluster with the embedding groups, separately. If group I is chosen to be the cluster, with state a, described by any MC wave function expansion, the effective total cluster energy can be written as [24]:

$$(\mathrm{H^I}(aa))^{eff} = \langle\Phi_a^I|\hat{H}_{eff}^I|\Phi_a^I\rangle + \sum_{S\neq I}\left\{\langle\Phi_b^S| - \sum_{j\in S}\sum_{\mu\in I}\frac{Z_\mu}{|\mathbf{r_j}-\mathbf{R}_\mu|}|\Phi_b^S\rangle + \sum_{\mu\in I}\sum_{\nu\in S}\frac{Z_\mu Z_\nu}{|\mathbf{R}_\mu-\mathbf{R}_\nu|}\right\} \tag{2.5}$$

where

$$\begin{aligned}\hat{H}_{eff}^I &= \sum_{i\in I}\left\{-\frac{1}{2}\nabla_i^2 + \sum_{\mu\in I}\frac{Z_\mu}{|\mathbf{r_i}-\mathbf{R}_\mu|}\right\} + \\ &\sum_{S\neq I}\left\{-\sum_{i\in I}\sum_{\nu\in S}\frac{Z_\nu}{|\mathbf{r_i}-\mathbf{R}_\nu|} + \sum_{i\in I}[\hat{J}^S(i) - \hat{K}^S(i) + \hat{P}^S(i)]\right\} + \\ &\sum_{i>k\in I}\frac{1}{|\mathbf{r_i}-\mathbf{r_k}|} + \sum_{\mu>\nu\in I}\frac{Z_\mu Z_\nu}{|\mathbf{R}_\mu-\mathbf{R}_\nu|}\end{aligned} \tag{2.6}$$

In the expressions above the Greek letters are reserved for nuclei, Z is the nuclear charge, and $\hat{J}^S$ and $\hat{K}^S$ are the effective one-electron Coulomb and exchange operators.

The interaction between the cluster electrons and the other electron groups is contained in the first term of Eq. (2.5). Those interactions are basically introduced as additional terms to the one-electron cluster hamiltonian $\hat{h}^I$,

$$\hat{V}^S(i) = \underbrace{-\sum_{\nu\in S}\frac{Z_\nu - N_\nu}{|\mathbf{r_i}-\mathbf{R}_\nu|}}_{\hat{V}^S_{lr-Coul}(i)} \underbrace{-\sum_{\nu\in S}\frac{N_\nu}{|\mathbf{r_i}-\mathbf{R}_\nu|} + \hat{J}^S(i)}_{\hat{V}^S_{sr-Coul}(i)} \underbrace{-\hat{K}^S(i)}_{\hat{V}^S_{exch}(i)} \tag{2.7}$$

The $\hat{V}^S(i)$ operator is a potential energy operator which contains the interaction of a cluster electron i with the frozen electron group S. This operator can be decomposed

into different contributions of the embedding group S, namely the Coulomb potential is separated into long- and short-range components and the non-local exchange operator $\hat{K}^S(i)$ constitutes the exchange contribution to $\hat{V}^S(i)$ (see Eq. (2.7)). N_ν is a number which is introduced to ensure the separation of the electrostatic Coulomb potential into long- and short-range components [24,53]. It is usually chosen to be equal to the number of electrons associated with the nuclei ν that belong to the embedding electron group S. The electrostatic Coulomb potentials include the attractions between the cluster electrons and the nuclei ν where the latter are arbitrary assigned to a particular embedding group S. The assignment of a number of nuclei ν to a specific embedding electron group S is arbitrary [24]. Next, the embedding operator, $\hat{V}^S(i)$, in Eq. (2.7) is replaced by a model potential $\hat{V}^{S,MP}(i)$. The $\hat{V}^S_{lr-Coul}(i)$ operator is replaced by the point charge potential corresponding to the long-range Coulomb potential. The short-range Coulomb potential, which includes the deviations from the point charge potential, is substituted by an analytical function [24],

$$V^{S,MP}_{sr-Coul}(i) \;=\; \sum_l \frac{B^S_l e^{-\alpha^S_l \mathbf{r_i}^2}}{\mathbf{r_i}} \tag{2.8}$$

in case the S electron group is atomic. The set of parameters (B^S_l, α^S_l) is obtained using a least-square fitting to $\hat{V}^S_{sr-Coul}(i)$, where the latter is computed with the wave function Φ^S_b. For polyatomic electron groups S, one adopts the same model potential representation of $\hat{V}^S_{sr-Coul}(i)$ as that of the non-local exchange operator, $\hat{V}^S_{exch}(i)$, namely, their corresponding spectral representations in the primitive basis $\{|p^S\rangle\}$ used for the wave function of S,

$$\begin{aligned} \hat{V}^{S,MP}_{sr-Coul}(i) &= \hat{\Omega}^S \hat{V}_{sr-Coul}(i) \hat{\Omega}^S \\ \hat{V}^{S,MP}_{exch}(i) &= \hat{\Omega}^S \hat{V}_{exch}(i) \hat{\Omega}^S \end{aligned} \tag{2.9}$$

where the projection operator $\hat{\Omega}^S$ is given by

$$\begin{aligned} \hat{\Omega}^S &= \sum_p \sum_q |p^S\rangle (S^S)^{-1}_{pq} \langle q^S| \\ S^S_{pq} &= \langle p^S | q^S \rangle \end{aligned} \tag{2.10}$$

The expressions in Eq. (2.8) and Eq. (2.9) constitute the AIMP representation of the embedding operator $\hat{V}^S$. The AIMP of $\hat{V}^S$ is obtained by optimizing in a SCF procedure the group wave function of S (most often an atom/ion) in the effective field of the remaining ions in the crystal. To obtain the embedding wave functions Φ^S_b and the cluster wave function Φ^I_a one needs to apply the restricted variational principle of Huzinaga [30, 53]. As mentioned above, the embedding electron groups S are usually taken in their ground state. The ground state wave function Φ^S_0 of the embedding groups S can be most often described by a single configurational state function (CSF). One employes the restricted variational principle of Huzinaga which implies the introduction of a shift operator $\hat{P}^S$ in the expression for the AIMP representation of $\hat{V}^S$ in order to prevent occupation of orbitals of the embedding Φ^S_0

in the configurational expansion of the wave function Φ_a^I of the cluster. The shift operator is given as [24],

$$\hat{P}^S(i) \quad = \quad \sum_{g\in S}^{occ} |\psi_g^S\rangle - x_g^S \epsilon_g^S \langle\psi_g^S| \tag{2.11}$$

where ϵ_g^S and ψ_g^S are the orbital energies and the occupied orbitals in which the wave function Φ_0^S is expanded. x_g^S is a projection factor which has been shown to have a value of 2 for the case of closed-shell electron groups at the Hartree-Fock level [48]. Various values of the factor can be used [49] to maintain the orthogonality conditions between the cluster wave function and the wave functions of the embedding groups in case the latter are represented by bare AIMPs without orthogonalizing basis functions.

The number of embedding groups S in the crystal is infinite and this requires an infinite number of embedding potentials $\sum_{S(\neq I)}[V_{lr-Coul}^{S,MP}(i)+\hat{V}_{sr-Coul}^{S,MP}(i)+\hat{V}_{exch}^{S,MP}(i)+\hat{P}^S(i)]$ to be added to the one-electron cluster Hamiltonian in order to obtain a correct expression for the effective one-electron cluster Hamiltonian. In practice however, the embedded cluster calculations are carried out by including the long- and short-range AIMP embedding operators for the nearest and next-nearest embedding ions of the cluster while preserving only the long -range Coulomb potential associated with the distant ions. The AIMP form of the effective cluster Hamiltonian, after replacing the effective embedding operators by their model potential representations, is:

$$\hat{H}_{AIMP}^C(1,...,N_I) \quad = \quad \sum_{i\in I}\left\{ -\frac{1}{2}\nabla_i^2 - \sum_{\mu\in I}\frac{Z_\mu}{|\mathbf{r_i}-\mathbf{R}_\mu|} + [V_{lr-Coul}^S(i) + \hat{V}_{sr-Coul}^{S,MP}(i) + \right.$$
$$\left. \hat{V}_{exch}^{S,MP}(i) + \hat{P}^S(i)]\right\} + \sum_{i>j\in I}\hat{g}(i,j) \tag{2.12}$$

Note, that compared to the effective cluster operator before replacing the embedding one-electron operators by their AIMP forms, its AIMP representation in Eq. (2.12) includes explicitly only nuclear attractions associated with the cluster nuclei. The ones associated with the 'embedding' nuclei are collected in the long-range Coulomb model potential.

Finally the second and the third terms in Eq. (2.5) express the interactions of the cluster nuclei with the electrons and nuclei of the embedding groups. These terms remain constant provided that the nuclei of the embedding groups are clamped and the electron groups are frozen. More details of the analysis on the effective cluster and cluster-embedding matrix elements are provided in reference [46].

The studies of local excitations and core and valence ionizations [16,17,28] in transition metal compounds have demonstrated that the AIMPs are good representation of the effect of the embedding crystal. In some cases however, for example ionized states in transition metal oxides [16], the bare potentials must be augmented with so called orthogonalizing basis functions in order to maintain the strong orthogonality conditions between cluster wave function and embedding wave functions (see also *Chapters 6 and 7*).

The AIMP embedded cluster approach performs equally well for clusters with anion or cation peripherial ions when studying the energy potential surfaces of the ground and excited states. An important advantage of this local approach is that the cluster properties converge faster with the cluster size.

The Total Ion Potential Technique The Total Ion Potentials (TIPs) are basically effective core potentials without basis functions. They are sometimes employed to represent the cations external to the cluster. The interactions of the cluster electrons with the external ions are incorporated through the effective one-electron Hamiltonian of the cluster. Analogous to the AIMP approach the expression for the cluster effective energy contains matrix elements of the embedding operators which are approximated in the present study using the large effective core potentials by Hay and Wadt [25].

To generate effective core potentials Hay and Wadt obtain first numerical Hartree-Fock (relativistic or non-relativistic) atomic valence orbitals from which they derive so called smooth nodeless pseudo-orbitals, so that the latter are close enough in the valence region of an atom to the initial numerical Hartree-Fock orbitals [25]. Then Hay and Wadt generate numerically the effective core potentials U_l for each angular momentum quantum number l using the valence pseudo-orbitals ϕ_l^{PO}. Next the authors impose the condition that a ϕ_l^{PO} is a solution of the atomic Hartree-Fock equations in the field of U_l plus the core Coulomb and exchange operators, $\hat{J}^c$ and $\hat{K}^c$, and the valence Coulomb and exchange operators $\hat{J}^v$ and $\hat{K}^v$, with the same orbital energy as the initial numerical Hartree-Fock orbital ϕ_l.

Winter, Pitzer and Temple have employed first the effective core potentials as TIPs in cluster calculations when studying the properties of Cu^+ impurities in NaF [52]. Although it seems rather crude at first sight to approximate the charge distribution of an ion (atom), external to the cluster, by an effective potential designed for the core electrons of that external ion, the TIP technique often gives a satisfactory description of the short-range interaction between the cluster and nearest surrounding ions. A drawback of the embedding is that it is restricted only to external cations.

Long-Range Lattice Polarization The embedding model potentials, discussed above, represent the effect of the embedding on the cluster under the condition of a frozen electron distribution for the embedding groups. This means that the embedding potentials are derived using frozen wave functions for the embedding groups, where the latter are obtained as they occur in a perfect cluster lattice. The lattice response to the charge distribution within the cluster region due to the presence of, for example, a defect or an ionization process, can not be accounted for in the frozen electron distribution approximation. The presence of charged defects or impurities in the crystal is usually accompanied by long-range dipole polarization and large local distortions, respectively. The local distortions that occur in the presence of an impurity may extend in some cases beyond the cluster region [24]. The polarization effects in the rest of the crystal may have a rather long range in the case, for example, of ionization processes which are object of study in the core-level spectroscopy. The

lattice polarization, on the other hand, affects back the electron distribution within the cluster region and hence, the local properties under investigation. It seems natural that a self-consistent treatment should be applied in which the external potential which the cluster experiences should be updated in order to incorporate the response of the surrounding polarized crystal. One alternative in the case of an ionic solid is to consider the embedding crystal as built from discrete polarizabilities and embed the cluster in a set of point polarizabilities. Then one may invoke the so-called Direct Reaction Field (DRF) method [55–59] in order to solve self-consistently the problem of a cluster embedded in a set of polarizable entities. This method has been applied to the solute-solvent interactions [58, 59] and to incorporate the long-range polarization effects on the computed ionization energies and electron affinities in NiO [44]. Janssen and Nieuwpoort have studied the band gap of NiO, i.e. the related ionization energies and electron affinities, by employing a $[NiO_6]$ embedded cluster [44]. Their study has shown that the *3d* ionization energy at the Ni^{2+} site is strongly dependent of the bulk polarization. We come back to this issue in Chapter 7, where we study the lowest ionization energies at the Ni^{2+} and O^{2-} sites in NiO.

The cluster model is particularly well suited for the studies of the local electronic structure of defects, local excitations and impurities in crystals [31, 33, 64, 87–89] as well as localized electronic states in transition metal materials (see *e.g.* [2–4, 44]). Employing the periodic approach for isolated defects and impurities in infinite lattices requires the introduction of a large unit cell to minimize the possible interaction of the defects localized at two neighbouring unit cells. Neutral defects in bulk LiF have been studied by Nada *et al* using an *ab initio* Hartree-Fock perturbed-cluster embedding scheme [51]. This study has shown that even in the case of neutral defects, important short-range polarization effects occur.

2.2 Wave function based theoretical approaches

Solving the time-independent Schrödinger equation for a N- electron system in the non-relativistic approximation is a starting point in most quantum mechanical approaches. This equation reads,

$$\hat{H}\Psi(\mathbf{x_1}, \mathbf{x_2}, ..., \mathbf{x_N}) = E\Psi(\mathbf{x_1}, \mathbf{x_2}, ..., \mathbf{x_N}) \tag{2.13}$$

where $\Psi(\mathbf{x_1}, \mathbf{x_2}, ..., \mathbf{x_N})$ is the exact many-electron wave function, E is the associated total electronic energy and $\hat{H}$ is the Hamiltonian operator. $\Psi(\mathbf{x_1}, \mathbf{x_2}, ..., \mathbf{x_N})$ is a function of the space and spin electron coordinates, unified in the $\mathbf{x}$-variables. Solving this equation, is in practice, possible only for few simple one-electron systems, such as the H atom and the H_2^+ molecule- ion. This is so because the wave function $\Psi(\mathbf{x_1}, \mathbf{x_2}, ..., \mathbf{x_N})$ describes the complicated correlated motion of all N electrons. Thus, approximations to the solutions of the Schrödinger equation are needed.

In the following sections we will use the second quantization formalism.

The Schrödinger equation in (2.13) in the Fock space is given as,

$$\hat{H}|\Psi\rangle = E|\Psi\rangle \tag{2.14}$$

The most common approach to an approximate solution of the Schrödinger equation is to expand the approximate N- electron wave function $|\Phi\rangle$ as a linear combination of Slater determinants (SD), $|i\rangle$, where the latter are built as N-electron normalized antisymmetrized products within a set of orthonormal spin-orbitals $\phi_{p\sigma}$,

$$|\Phi\rangle = \sum_i C_i |i\rangle \tag{2.15}$$

Provided that we work in the limit of a complete set of spin-orbitals we may approach the exact solution of the Schrödinger equation close enough, at the cost of an infinite determinantal expansion.

In the Born-Oppenheimer approximation and in the absence of external fields, the spin-free non-relativistic Hamiltonian is expressed as a sum of one- and two-electron operators, $\hat{h}$ and $\hat{g}$ and a nuclear-nuclear repulsion term h_{nuc}. The operators are expressed in terms of the set of the orthonormal spin-orbitals $\phi_{p\sigma}$ [65],

$$\hat{H} = \underbrace{\sum_{pq} h_{pq}\hat{E}_{pq}}_{\hat{h}} + \underbrace{\frac{1}{2}\sum_{pqrs} g_{pqrs}(\underbrace{\hat{E}_{pq}\hat{E}_{rs} - \delta_{qr}\hat{E}_{ps}}_{e_{pqrs}}) + h_{nuc}}_{\hat{g}} \tag{2.16}$$

where

$$\begin{aligned} e_{pqrs} &= \sum_{\sigma\tau} \hat{a}^\dagger_{p\sigma}\hat{a}^\dagger_{r\tau}\hat{a}_{s\tau}\hat{a}_{q\sigma} \\ \hat{E}_{pq} &= \sum_{\sigma} \hat{a}^\dagger_{p\sigma}\hat{a}_{q\sigma} \end{aligned} \tag{2.17}$$

are the two-electron excitation operator and one-electron excitation operator, respectively. The one- and two-electron integrals are given here as,

$$\begin{aligned} h_{pq} &= \int \phi_p(\mathbf{r})(-\frac{1}{2}\nabla^2 - \sum_\mu \frac{Z_\mu}{\mathbf{r}_\mu})\phi_q(\mathbf{r})d\mathbf{r} \\ g_{pqrs} &= \int\int \frac{\phi^*_p(\mathbf{r_1})\phi^*_r(\mathbf{r_2})\phi_q(\mathbf{r_1})\phi_s(\mathbf{r_2})}{|\mathbf{r_1} - \mathbf{r_2}|} d\mathbf{r_1}d\mathbf{r_2} \end{aligned} \tag{2.18}$$

The integration is only over the spatial coordinates because the orthogonality of the spin functions in the spin-orbitals leads to a cancelation of most of the terms in the initial expression for the matrix elements of the spin-free two-electron operator $g_{p\sigma,q\tau,r\mu,s\nu}$ In addition, the summations over the spin variables in Eq. (2.17) remove the spin-index dependences of $\hat{h}$ and $\hat{g}$.

In practice it is not possible to work with a complete set of (one-electron wave functions) spin-orbitals and to construct a wave function expansion in a complete (infinite) set of SDs. Therefore different methods have been developed to provide an approximate solution to the Schrödinger equation within a finite one-electron basis set and a truncated SD expansion.

Within the Hartree-Fock (HF) approximation [61], the N-electron wave function is approximated by a single SD (unrestricted HF) or a single spin- and symmetry-adapted configuration state function (CSF). The HF wave function and its energy are obtained by employing the variational theory in order to minimize the expectation value of the Hamiltonian with respect to the spin-orbitals. The one-electron wave functions $\phi_{p\sigma}$ are usually expanded into a discrete set of basis functions which leads to so-called Hartree-Fock-Roothaan equations [62]. For further discussion on the (restricted and unrestricted) Hartree-Fock approach the reader is referred to [46, 65, 66].

Configuration State Functions

The exact many-electron wave function is considered to be an eigenfunction of the non-relativistic and spin-free electronic Hamiltonian within the Born-Oppenheimer approximation. $\hat{H}$ commutes with the spin operators $\hat{\mathcal{S}}^2$ and $\hat{\mathcal{S}}_z$ and hence, the many-electron wave function must be also a spin eigenfunction with quantum numbers S and M. When searching for an approximation to this exact wave function, most often one carries out the optimization in a restricted space, which consists of spin eigenfunctions with quantum numbers S and M. The Slater determinants are not in general eigenfunctions of $\hat{\mathcal{S}}^2$ though, it is possible to generate eigenfunctions by determining linear combinations of Slater determinants. Likewise, one sometimes needs to determine linear combinations of SD in order to let them transform according to one of the irreducible representations of the symmetry group. The CSF is a spin- and symmetry- adapted linear combination of Slater determinants, i.e. eigenfunction of the operators $\hat{\mathcal{S}}^2$ and $\hat{\mathcal{S}}_z$ and transforming according to one of the irreducible representations of the symmetry group of the system. In constructing the CSFs, determinants which belong to the same *orbital configuration* are combined. An *orbital configuration* contains all SDs with the same occupation number vectors of the orbital basis they are built of.

2.2.1 Multiconfigurational Self-Consistent Field Approach and Configuration Interaction

The presence of several important electronic configurations in the wave function expansion is a common case for the ground and excited states of transition metal oxides. The ground state of the ozone molecule and the dissociation of the nitrogen molecule are other representative examples. The single-configuration Hartree-Fock (HF) method [60–62] is by construction unable to describe multi-configurational electron systems. Perturbation methods as second- or higher-order Møller-Plesset theory are designed to improve the description based on HF theory. This approach allows for obtaining size-extensive correlation energies when the system is represented mainly by a single electronic configuration. The orbitals generated self-consistently within HF theory may be inappropriate for the MC system. The MCSCF method [63] then provides a natural solution to the problems.

Within the framework of the MCSCF method the wave function is written as a linear combination of Slater determinants (SD) $|i\rangle$ or spin- and symmetry-adapted linear combinations thereof, denoted configuration state functions (CSFs) $|j\rangle$,

$$|\kappa, \mathbf{C}\rangle = e^{-\hat{\kappa}} \sum_i C_i |i\rangle = e^{-\hat{\kappa}} \sum_j C_j |j\rangle \tag{2.19}$$

In order to construct the wave function, one optimizes variationally the expectation value of the energy

$$E = min_{\kappa,\mathbf{C}} \frac{\langle \kappa, \mathbf{C}|\hat{H}|\kappa, \mathbf{C}\rangle}{\langle \kappa, \mathbf{C}|\kappa, \mathbf{C}\rangle} \tag{2.20}$$

with respect to the parameters of the orbital-rotation operator $e^{-\hat{\kappa}}$ and the CI coefficients C_i or C_j. In practice, the parametrization of the MCSCF model Eq. (2.19) is the same as that of the CI model, except for the presence of the orbital-rotation operator. The CI wave function is constructed as a linear combination of SD or CSFs and the coefficients in the CI expansion are determined by a variational optimization of the expectation value of the energy but only with respect to C_i or C_j. The presence of $e^{-\hat{\kappa}}$ in the MCSCF wave function allows for obtaining orbitals adapted to the CI expansion. MCSCF may be also used as a generator of a reference wave function for more elaborate electronic structure calculations [65]. If the CI expansions must contain more than a single CSF for the proper description of the wave function, the non-dynamical (static) electron correlation effects are considered to be significant.

In the case of the spin-free non-relativistic Hamiltonian which commutes with the total and projected spin operators $\hat{\mathcal{S}}^2$ and $\hat{\mathcal{S}}_z$, one usually requires wave functions with well defined spin quantum numbers.

The optimization of the expansion coefficients of the CSFs $|j\rangle$ in the MCSCF wave function can be performed by using a configuration vector which is orthogonal to the MCSCF initial reference state $|0\rangle = \sum_j C_j^{(0)} |j\rangle$ [65],

$$|\mathbf{C}\rangle = e^{-\hat{\kappa}} \frac{|0\rangle + \hat{P}|\mathbf{c}\rangle}{\sqrt{1 + \langle \mathbf{c}|\hat{P}|\mathbf{c}\rangle}} \tag{2.21}$$

with a projection operator $\hat{P} = 1 - |0\rangle\langle 0|$ and the state $|\mathbf{c}\rangle = \sum_i c_j |j\rangle$ contains the free parameters c_j. $|0\rangle$ is the starting normalized approximation to the wave function of an electronic state. Using this parametrization of the MCSCF wave function one carries out the variations in the spin-orbital space and in the configuration space in a SCF procedure to obtain the best approximation to the wave function and energy of the electronic state. Efficient methods have been developed for the optimization of the MCSCF wave function. One of the main schemes employed in the modern quantum mechanical packages is based on modifications of the full second-order Newton-Raphson method [65,66]. The second optimization approach is the so-called super-CI approach [66, 72]. The Newton- Raphson method usually shows a fast convergence of the optimization procedure provided that the initial wave function is a reasonable

start, however precautions must be taken to prevent from a convergence to a saddle point or maxima. In the super-CI approach, each step in the optimization procedure is faster, however more steps are needed to achieve a convergence. Owing to the extensive description of both optimization schemes in textbooks as [66] we do not discuss them here.

CASSCF and RASSCF

In this section we discuss a method for incorporation of the static electron correlation or so called near-degeneracy correlation which is related to the presence of more than one important CSFs in the wave function expansion of a particular state. This occurs because of the near-degenerate energies of two or more electronic configurations. Different kinds of MCSCF wave functions may be constructed but the most used ones are based on the Complete Active Space (CAS) SCF method [70]. Within this method the (spin-) orbital space is partitioned into three subspaces: inactive, active and secondary, or virtual. The orbitals which constitute the inactive space remain doubly occupied in all configurations of the MC wave function expansion. The orbitals in the secondary or virtual subspace remain unoccupied in all configurations. The active space contains a fixed number of electrons which are distributed over the active orbitals in all possible ways, restricted by the spin and spatial symmetry of the CASSCF wave function.

The Restricted Active Space (RAS) SCF method [71, 72] has been viewed as an extension of the CASSCF method. The (spin-) orbital space contains again inactive and secondary spaces, defined as within CASSCF, but in addition, the active space is divided further into three subspaces RAS1, RAS2 and RAS3. In constructing the different RAS subspaces, one imposes restrictions on the maximum number of holes or electrons, allowed in the RAS1 and RAS3 sub-spaces, respectively. In the RAS2 space all possible configurations, arising from the distribution of the active electrons, that are not in RAS1 and RAS3, over the RAS2 orbitals are included.

In the CASSCF approach one performs full CI within the active space, and thus, the redundant active-active orbital rotations need not to be considered. The additional subdivision of the active space within RASSCF introduces active-active orbital rotations between the three RAS spaces which are not redundant and thus, have to be considered. An advantage of the RASSCF approach is the possibility to use more active orbitals. The multi-reference (MR) singles and doubles (SD) wave function is a RASSCF wave function, which has the CAS space as a reference space and at most two holes and two electrons in RAS1 and RAS3, respectively. The RASSCF wave functions are suited to incorporate not only the non-dynamical correlation effects but also dynamical correlation effects.

Efficient methods have been developed for performing the RASSCF, RASCI and CASSCF and CASCI calculations, based on SD-based CI algorithms [71].

2.2.2 Complete Active Space Second-Order Perturbation Theory

The dynamical correlation effects which are due to the two-electron interactions in the cusp region ($\mathbf{r_{12}} \approx 0$) are often recovered in a post-MCSCF (or post- HF) calculation. A common method used to treat those effects in the case of a MC reference wave function is multi-reference CI (MRCI). The MRCI wave function is a CI expansion of all excited configurations of a certain order (singly-, doubly-, triply- and so on excited configurations) generated from a set of MC reference wave functions. An alternative to MRCI is the many-body perturbation theory, (MBPT), which main advantage is the smaller computational expense.

The most often used MBPT for the calculation of the dynamical correlation energy is the second-order MBPT. We use in the current research a second-order perturbation approach to the dynamical electron correlation based on a reference CASSCF [72] wave function as it has been developed by Andersson, Malmqvist and Roos [81]. This method aims at the calculation of the second-order estimate of the dynamical correlation energy and the first-order estimate of the wave function. The starting point in this theory is to define an appropriate zero-order Hamiltonian operator and a configuration space to expand the first-order wave function, so-called first-order interaction space.

If one extends the one-electron Fock operator $\hat{f}$ which is given in the orbital basis within the Møller -Plesset second-order perturbation theory to the CASSCF reference wave function, $|0\rangle$, one obtains the following form of $\hat{f}$ [65,81], the CASSCF Fock operator,

$$\hat{f} = \sum_{pq} f_{pq}\hat{E}_{pq} = \frac{1}{2}\sum_{pq}\sum_{\sigma}\langle 0|[\hat{a}^{\dagger}_{q\sigma},[\hat{a}_{p\sigma},\hat{H}]]_{+}|0\rangle\hat{E}_{pq} \tag{2.22}$$

In case the reference CASSCF wave function is reduced to the closed-shell HF wave function, the CASSCF Fock operator reduces to the Fock operator in the Møller - Plesset theory. The CASSCF wave function is not an eigenfunction of the CASSCF Fock operator, but one can still construct a zero-order operator $\hat{H}_0$, which has the reference, zero-order, CASSCF wave function as an eigenfunction. This can be done by using a projection operator onto the reference wave function $|0\rangle$, $\hat{P}_0$=$|0\rangle\langle 0|$, and orthogonal projection operators $\hat{P}_K$, $\hat{P}_{SD}$, $\hat{P}_X$, onto the rest of the configuration space. $\hat{H}_0$ has the form [65,81],

$$\hat{H}_0 = \hat{P}_0\hat{f}\hat{P}_0 + \hat{P}_K\hat{f}\hat{P}_K + \hat{P}_{SD}\hat{f}\hat{P}_{SD} + \hat{P}_X\hat{f}\hat{P}_X \tag{2.23}$$

The first-order wave function $|0^1\rangle$ is constructed using a so-called internally contracted scheme as a linear combination of all CSFs connected to all single and double excitations from the reference CASSCF wave function $|0\rangle$ [65],

$$|0^1\rangle = \sum_{pq} C^1_{pq}\hat{E}_{pq}|0\rangle + \sum_{pq\geqslant rs} C^1_{pqrs}(\hat{E}_{pq}\hat{E}_{rs} - \delta_{qr}\hat{E}_{ps})|0\rangle \tag{2.24}$$

where the $\hat{E}_{pq}$ are one-electron excitation operators. The use of the internally contracted scheme in the construction of $|0^1\rangle$ ensures a rather limited number of terms in the perturbation series.

On the other hand the internally contracted scheme leads to a rather complicated formalism which involves the construction of three-particle density matrices over the active space, needed in the evaluation of the second-order CASPT energy and the coefficients of the first-order CASPT wave function correction [65]. An alternative to the internally contracted scheme is to express the first-order wave function in terms of Slater determinants. However, this leads to computationally demanding very long perturbation series.

For further details on the CASPT2 formalism as well as on the use of different forms of the zero-order Hamiltonian in CASPT2 the reader is referred to [65, 83].

Finally, we comment on the breakdown of the CASPT2 approach in case of the presence of configurations in $\mathbf{C}^1$ with expectation values of $\hat{H}^0$ that are very close to or even lower than the expectation value of the reference wave function. If we write the first-order wave function and second-order correction to the energy in the following forms, disregarding first the correction μ,

$$\tilde{E}^2 = -\sum_j \frac{|\langle j|\hat{H}^{(1)}|0\rangle|^2}{\epsilon^j - E^{(0)} + (\mu)} \qquad \hat{H} = \hat{H}^0 + \lambda \hat{H}^{(1)}$$

$$\tilde{C}^1_j = -\sum_j \frac{\langle j|\hat{H}^{(1)}|0\rangle}{\epsilon^j - E^{(0)} + (\mu)}$$

the energy denominators of E^2 and C^1_j become very small when the expectation values of a certain $|j\rangle$ and $|0\rangle$, ϵ^j and $E^{(0)}$ become close. This causes a breakdown of the perturbation theory. As shown by de Graaf *et al.* in extensive studies of the low-energy electronic excitations, magnetic couplings and core-hole excitations in insulating *3d* TM oxides [2, 10, 11, 28] the TM oxides are very susceptible to this breakdown. In the case of non Fock-type zero-order Hamiltonians, $\hat{H}^0$, so called intruder states may be contained in the configuration space of the first-order wave functions. When the interaction matrix elements between the intruder state and the reference wave function, in the expression for the first-order wave function, are large, the best solution is to extend the reference wave function so to include the intruder state. In the cases of small interaction matrix elements but conserved (near -) degeneracy between the intruder and reference state, one may apply the so-called level-shift technique, developed by Roos and Andersson [84]. The energy of the intruder state and all other configurations in the first-order interaction space is shifted up artificially by adding a value μ to the expectation value of $\hat{H}^0$ of this intruder state (see Eq. (2.25)),

$$E^2 - \tilde{E}^2 = \mu(1 - \frac{1}{\tilde{w}}) \tag{2.25}$$

where $\tilde{w}$ is the weight of the CASSCF wave function in the first-order wave function after applying the level shift μ (see [84]). The first-order wave function looses its

significance after applying the correction shift, but the second-order energy can be corrected back for the applied shift (see [84]), More details on the use of the technique can be found, for example, in references [84]. In Chapter 6 we come back to this issue in the context of the study of the lowest valence excitations in cubic and orthorhombic $LaMnO_3$ where we discuss as well a new level shift technique denoted as imaginary level shift technique [85].

2.3 State Interaction

The CASSI and RASSI [73] methods enable an efficient calculation of matrix elements of one- and two-electron operators and one- and two-electron transition density matrices, respectively for two CASSCF or RASSCF wave functions, each expressed in its own optimized orbitals. The ground and excited electronic states of various molecular and crystal structures have been described with a good accuracy with CASSCF and RASSCF wave functions (see e.g. [3, 5, 6, 16–18, 80]). Transition dipole moments and oscillator strengths, on the other hand, involve two different electronic states. Evaluating these quantities requires the computation of the matrix elements of one-electron-operators, such as the dipole transition moments, between wave functions expressed in different mutually non-orthogonal orbital basis. The computation of, for example, oscillator strengths accurately requires high quality wave functions, but those can be obtained in most cases best if the different wave functions, involved in the transition, are expressed in their own orbital basis. If such wave functions are obtained in separate CASSCF or RASSCF calculations, they are in general non-orthogonal and interacting. Better wave functions are then obtained by solving the secular equations within the space spanned by the non-orthogonal and interacting wave functions [73]. In order to do so, one must construct and evaluate the Hamiltonian matrix elements and overlap integrals between those non-orthogonal wave functions.

To compute the matrix elements of the one-electron operators, relevant to the transition strengths, as well as the Hamiltonian matrix elements and overlap integrals between the interacting non-orthogonal wave functions, Malmqvist developed an efficient scheme based on non-unitary orbital transformations [75]. The development of the scheme was directed to the computation of the one- and two- electron transition density matrices for two MC wave functions but it became an efficient and powerful tool for the calculation of arbitrary one- and two-electron matrix elements between wave functions expressed in different orbital basis, X and Y. Let us first assume that the two sets are orthonormal but mutually non-orthogonal. The original non-orthogonal MC wave functions are then given by the following CI expansions,

$$
\begin{aligned}
|\mathbf{C^X}\rangle &= \sum_i C_i^X |i^X\rangle \\
|\mathbf{C^Y}\rangle &= \sum_i C_i^Y |i^Y\rangle
\end{aligned}
\tag{2.26}
$$

where $|i^X\rangle$ and $|i^Y\rangle$ are the two different CSF bases, constructed from two different orbital sets φ^X and φ^Y. Both sets of CSF are constructed by the same spin-coupling

scheme which is otherwise arbitrary. The matrix elements of the one- ($\hat{F}$) and two-electron ($\hat{G}$) operators, formed between $|\mathbf{C^X}\rangle$ and $|\mathbf{C^Y}\rangle$ are [65, 66, 73–75][a]:

$$\langle \mathbf{C^X}|\hat{F}|\mathbf{C^Y}\rangle = \sum_{ij} C_i^X C_j^Y \sum_{pq} A_{pq}^{ij} \langle \varphi_p^X|\hat{f}|\varphi_q^Y\rangle$$

$$\langle \mathbf{C^X}|\hat{G}|\mathbf{C^Y}\rangle = \frac{1}{2}\sum_{ij} C_i^X C_j^Y \sum_{pqrs} A_{pqrs}^{ij} \langle \varphi_p^X \varphi_r^X|\hat{g}|\varphi_q^Y \varphi_s^Y\rangle \tag{2.27}$$

where

$$\hat{F} = \sum_{k}^{nelectrons} \hat{f}(k) = \sum_{pq} f_{pq} \underbrace{\hat{a}_p^\dagger \hat{a}_q}_{\hat{E}_{pq}} \quad f_{pq} = \langle \varphi_p^X|\hat{f}|\varphi_q^Y\rangle$$

$$\hat{G} = \frac{1}{2}\sum_{k\neq l} \hat{g}(k,l) = \frac{1}{2}\sum_{pqrs} g_{pqrs} \underbrace{\hat{a}_p^\dagger \hat{a}_r^\dagger \hat{a}_s \hat{a}_q}_{\hat{E}_{pq}\hat{E}_{rs}-\delta_{qr}\hat{E}_{ps}} \quad g_{pqrs} = \langle \varphi_p \varphi_r|\hat{g}|\varphi_q \varphi_s\rangle$$

Analogously, the overlap matrix is also obtained [73, 75],

$$\langle \mathbf{C^X}|\mathbf{C^Y}\rangle = \sum_{ij} S_{ij}^{XY} C_i^X C_j^Y \tag{2.28}$$

The coefficients A and S will be specified below. It has been shown by Malmqvist [73, 75] for RASCI expansions that if the orbital overlap matrix is non-singular, other orbital sets φ^A and φ^B can be obtained from the original orthonormal but mutually nonorthogonal orbital sets φ^X and φ^Y using non-unitary orbital transformations. Provided that the non-singularity condition is imposed on the overlap matrix, two restricted orbital transformation matrices exist, $\underline{\underline{\Upsilon}}^{XA}$ and $\underline{\underline{\Upsilon}}^{YB}$ such that a biorthonormality condition between the transformed sets φ^A and φ^B holds,

$$\langle \varphi_p^A|\varphi_q^B\rangle = \delta_{pq}$$

The transformation of the original orthonormal (individually) orbital sets φ^X and φ^Y to some new biorthonormal basis, φ^A and φ^B, is at the cost of loosing the individual normalization of φ^A and φ^B. The transformation of the original orbital sets should be accompanied by a corresponding transformation of the CI expansion coefficients such that the new wave functions $|\mathbf{C^A}\rangle$ and $|\mathbf{C^B}\rangle$ are constructed from CSFs which span the same space as those CSFs, expressed in the original orbital sets, φ^X and φ^Y. Provided that the biorthonormality condition holds for orbital sets φ^A and φ^B, the overlap matrix $\underline{\underline{S}}^{AB}$ becomes the unity matrix and the A_{pq}^{ij} and A_{pqrs}^{ij} are the sparse sets of one- and two-electron coupling coefficients, encountered in the conventional case of wave functions expanded in a common set of CSFs, where the latter are built from a common set of orthonormal orbitals (see [73] and [75]). The coupling

[a] In the following expressions we work with spin-free operators, provided that the trivial summation over the spin variables have been carried out properly

coefficients in the biorthonormal CSF basis have the form [75],

$$A^{ij}_{pq} = \langle i^A | \hat{E}_{pq} | j^B \rangle$$
$$A^{ij}_{pqrs} = \langle i^A | \hat{E}^B_{pq} \hat{E}^B_{rs} - \delta_{qr} \hat{E}^B_{ps} | j^B \rangle$$

A^{ij}_{pq} are invariant under orbital transformations and take values 0 or ± 1 (CAS and RAS wave functions) as they do in the case of one orthonormal orbital basis for both $|\mathbf{C^A}\rangle$ and $|\mathbf{C^B}\rangle$. The one- and two-electron transition density matrices in biorthonormal orbital bases A and B have been expressed as the transition values of the spin-free singlet excitation operator $\hat{E}^B_{pq}$, and two-electron excitation operator $\hat{e}_{prqs}$, defined only in the basis B, respectively [75],

$$\Gamma^{AB}_{pq} = \langle \mathbf{C^A} | \hat{E}^B_{pq} | \mathbf{C^B} \rangle = \sum_{ij} C^A_i C^B_j A^{ij}_{pq}$$
$$\Gamma^{AB}_{pqrs} = \langle \mathbf{C^A} | \hat{E}^B_{pr} \hat{E}^B_{qs} - \delta_{rq} \hat{E}^B_{ps} | \mathbf{C^B} \rangle = \sum_{ij} C^A_i C^B_j A^{ij}_{pqrs}$$

The biorthonormality of φ^A and φ^B allows one to use the same formulae as those for the case of a single orthonormal orbital set for both wave functions. Thus the calculation of the Hamiltonian matrix elements and overlap integrals, as well as the matrix elements of various one-electron operators between non-orthogonal and interacting wave functions will be reduced to the calculation of the transition density matrices within the biorthonormal basis sets φ^A and φ^B. This is naturally accompanied by a transformation of the very original orbital sets φ^X and φ^Y into φ^A and φ^B and the corresponding CI expansions C^X_i and C^Y_j into C^A_i and C^B_j. The latter transformation has been performed using the orbital transformation matrices $\underline{\underline{\Upsilon}}^{XA}$ and $\underline{\underline{\Upsilon}}^{YB}$ [75]. The reader is referred to reference [75] for the detailed derivation of these matrices. In order to obtain proper orbital transformation matrices that preserve the CSF spaces of the CI expansions, one may perform an LU-factorization of $\underline{\underline{S}}^{XY}$ [73, 75]. In addition one needs to restrict the wave functions to RAS (CAS) expansions.

Once obtained, $\underline{\underline{\Upsilon}}^{XA}$ and $\underline{\underline{\Upsilon}}^{YB}$ are LU-factorized and the CI coefficients C^X_i and C^Y_j are transformed into the new CI coefficients C^A_i and C^B_j in a sequence of single-orbital transformations using the $\underline{\underline{L}}$ and $\underline{\underline{R}}^{-1}$ matrices of the LU-factorization and the one-electron coupling coefficients (see above). Next the transition density matrix elements are calculated using C^A_i and C^B_j and A^{ij}_{pq} and A^{ij}_{pqrs}. Finally the matrix elements of one- and two-electron integrals ($\langle \varphi^X_p | \hat{f} | \varphi^Y_q \rangle$ and $\langle \varphi^X_p \varphi^X_r | \hat{g} | \varphi^Y_q \varphi^Y_s \rangle$) are also transformed into the new basis set ($\langle \varphi^A_p | \hat{f} | \varphi^B_q \rangle$ and $\langle \varphi^A_p \varphi^A_r | \hat{g} | \varphi^B_q \varphi^B_s \rangle$) and the corresponding matrix elements of the one- and two-electron operators between the transformed wave functions, $|\mathbf{C^A}\rangle$ and $|\mathbf{C^B}\rangle$, are computed. This algorithm has been implemented in the quantum chemistry package MOLCAS [86] in a State Interaction code. The Hamiltonian matrix elements and overlap integrals are built between the original individually optimized RASSCF or CASSCF wave functions and the resulting secular equations are solved to yield a better set of non-interacting and orthonormal eigenfunctions expressed in terms of the original interacting and mutually

non-orthogonal wave functions,

$$|\mathbf{C}\rangle = \sum_m \Lambda_m^X |\mathbf{C_m^X}\rangle \tag{2.29}$$

Since the states are described by MCSCF wave functions, $|\mathbf{C_m^X}\rangle$ are many-electron basis functions consisting of more than one CSF, hence the approach is denoted as a state interaction (SI). In this context we mention another analogous approach, known as non-orthogonal CI (NOCI) [76, 77]. NOCI is based on expressing the final wave function as an optimized linear combination of non-orthogonal interacting wave functions, which are single CSFs. The expansion coefficients, Λ_m, of the NOCI wave function are obtained from solving the secular equations with the non-orthogonal single CSFs as a many-electron basis. The Hamiltonian matrix elements and overlap integrals between the non-orthogonal NOCI single CSF are evaluated by making use of an efficient scheme, named the Factorized Cofactor Method [76, 78]. In this thesis, we make an extensive use of the SI approach in order to obtain the Hamiltonian matrix elements and overlap integrals between localized individually optimized excited (ionized, added-electron) CASCI wave functions of large embedded clusters (super-clusters). These matrix elements are needed, for example, for the computation of double exchange parameters in manganites (see *Chapter 4*). Furthermore the matrix elements of the super-clusters are used to approximate the matrix elements of an extended system and then, employing those approximate matrix elements, to solve a non-orthogonal many-body tight-binding problem in order to obtain the eigenvalues and eigenvecotrs for the extended system (see *Chapters 3, 5 and 7*).

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